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THE ACTION OF HEAT AND MOISTURE ON LEATHER

PART III. THE EFFECT OF pH ON THE DETERIORATION OF VEGETABLE, CHROME, SEMICHROME, AND CHROME RETAN LEATHERS*

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ABSTRACT

Vegetable, chrome, semichrome, and chrome retan leathers were adjusted to various pH values in the range 2 to 9 and stored at 40°C. over water for 15 weeks.

The strength of the leathers as measured by buckle tear load was little affected by the adjustment of pH except when this was reduced below 3.0. Losses in strength during storage varied with the type of leather and with its pH. In general, in the range 4 to 8 pH had little effect on the losses of strength of chrome, vegetable, and semichrome leathers, but with the retan leather losses increased progressively with fall in pH. In this range the chrome leather lost no strength, the vegetable-tanned leather about 30%, the semichrome about 50%, and the chrome retan leather 10% at pH 8.0, increasing to 25% at pH 4.0. At lower pH values the losses in strength of the chrome and retan leathers increased sharply but those of the semichrome only slightly, while with the vegetable-tanned leather, losses were only increased at the lowest pH value (2.0). At this pH, however, the vegetable-tanned leather was extensively damaged after only two weeks' storage.

The leathers containing vegetable tan became progressively darker in color with increasing pH and tended to become cracky, but the chrome-tanned leather was relatively unaffected both in appearance and feel.

It is concluded that for resistance to storage the pH of the leather should be above 3.5, and even higher with chrome leather and retan leather. High pH values, however, lead to darkening of leathers containing vegetable tannins and to detannage of chrome leather, so that a limit must be set. In wear, the absorption of perspiration increases the pH of the leather, and this must also be borne in mind.

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INTRODUCTION

The effect of exposure of a variety of leathers to the action of moist heat has been described in Parts I and II (1,2). With the exception of chrome upper and gloving, most types of leather were found to lose strength, but only in extreme cases was there any marked increase in solubility. Although it was not possible to correlate losses in strength or change in other properties of any particular type of leather with its pH, it seems reasonable to assume that this must be a factor. In particular it would be expected that hydrolytic breakdown of the collagen would increase as the pH of the leather is decreased.

Little evidence on the effect of pH on the deterioration of leather under warm moist conditions appears to be available. The absorption of acid is known to accelerate the deterioration of upholstery and bookbinding leathers (3,4), and Kanagy, Seebold, Charles, and Cassel (5) have shown that in some cases raising the pH of chrome- and vegetable-tanned leather reduced deterioration under warm moist conditions.

The pH of any one type of leather may vary between quite wide limits, and in wear the absorption of perspiration may cause increases of two or more pH units. In order to be able to predict the probable behavior of a leather in wear it is, therefore, necessary to know how such changes in pH are likely to affect their resistance to the action of moist heat. Little information appears to be available on this point, though the work of Mitton and Wyatt (6) suggests that increases in pH due to synthetic and natural perspiration reduce losses in strength of vegetable, chrome, semichrome, and chrome retan leathers stored wet at 40°C. Four leathers, vegetable, chrome, semichrome, and chrome retan, have, therefore, been adjusted to various pH values, and their subsequent behavior on moist storage has been examined.

EXPERIMENTAL

Samples of vegetable, chrome, semichrome, and chrome retan leathers were adjusted to twelve pH values between 2 and 9 and stored at 40°C. over water for 15 weeks. The leathers were the same as those used in a previous experiment and have already been described (2). Samples 6″ x 1″ were cut from the britch end of the leathers in six blocks of twelve, and one sample from each block was allotted at random to each of the twelve treatments.

For adjustment of pH the samples were placed in a screw-top bottle of such depth that the samples just fitted below the shoulder. A volume of hydrochloric acid or sodium carbonate solution of the concentrations shown in Table I was added in the proportion of 1 ml. per gram of leather, and the bottles were rotated on their sides intermittently for 24 hours. During this time between 75% and 90% of the solutions were taken up by the leathers. The amounts of acid and alkali to be used to give a suitable range of pH were predetermined in a preliminary experiment. One percent p-nitrophenol was

TABLE I

CHANGE IN pH ON STORAGE

Treatment	Vegetable		Chrome		Semichrome		Retan	
	Before	After	Before	After	Before	After	Before	After
1. N HCl	1.90	2.30	2.32	2.42	1.92	2.19	1.86	2.14
2. 0.2N HCl	2.77	2.76	3.42	3.39	2.35	2.47	2.39	2.52
3. 0.1N HCl	3.38	3.12	3.74	3.37	2.63	2.69	2.64	2.68
4. Water	4.42	3.73	3.98	3.64	2.90	2.84	2.99	2.84
5. 0.05 N Na_2CO_3	4.60	3.66	4.16	3.33	3.14	2.88	3.12	2.94
6. 0.1N "	4.97	4.10	4.22	3.58	3.32	2.91	3.32	3.06
7. 0.15N "	5.14	4.26	4.31	3.83	3.56	3.20	3.42	3.15
8. 0.25N "	5.78	4.80	4.72	4.11	4.12	3.52	4.02	3.42
9. 0.4N "	6.12	5.26	5.92	4.27	5.24	3.98	4.75	3.95
10. 0.6N "	6.32	5.62	6.22	4.66	5.91	5.27	5.27	4.67
11. 0.8N "	6.68	5.87	6.99	5.17	6.64	6.04	6.66	5.80
12. 1.5N "	7.60	6.45	8.99	7.07	7.78	6.85	7.80	7.06

added to each of the solutions to reduce mold growth during subsequent storage.

The leathers were dried out on glass plates, and the strength (buckle tear load) was determined. The torn strips were cut off, and the pieces were used for the determination of pH of water extract and shrinkage temperature.

The leathers were then suspended over water in closed glass vessels and stored at 40°C. in an incubator for 15 weeks. After storage the pieces were dried out on glass plates, conditioned, and tested for buckle tear load, pH, and shrinkage temperature. They were also assessed for color and crackiness.

Methods.—Shrinkage temperatures were determined in water or 75% v/v glycerol-water mixture with specific gravity 1.194 using a counterweight of 10 g. The pieces were wetted first in water under reduced pressure, and the rate of heating was 2° per minute. The temperature at which shrinkage was first observed was taken as the shrinkage temperature. For pH of water extract, 2.5 g. leather in the form of pieces about 3 mm. sq. were extracted with 50 ml. distilled water for 48 hours with occasional shaking. Nitrogen soluble in 5M acetic acid was extracted and determined as described by Raistrick (2).

Buckle tear loads were determined by the usual procedure (7) after conditioning at 21°C. and 70% R.H. The three tests made on each sample were made at 1″ intervals from each other along the strip. The percentage loss in strength at each stage and the mean losses for the six samples were calculated. Percentage losses in strength of replicate varied by ±15%.

RESULTS

Effect of pH adjustments.—After treatment, the pH of water extracts of the leathers lay within the range 1.9 to 9.0. Although the values varied appreciably for the four types of leather, no obvious differences in their buffering capacities were apparent.

The appearance of the chrome-tanned leathers was little affected except that those given the more alkaline treatment had a greenish tinge. The leathers containing vegetable tan became progressively stiffer and darker in color with increasing alkalinity above pH 4.0. Even at the highest pH value, however, the leathers were not excessively stiff. These effects were most marked with the vegetable leather and least marked with the semichrome.

The strength of the leathers was not greatly affected by adjustment of the pH to values in the range 3 to 8, in most cases a slight increase being observed (*see Figs. 1–4*). At lower pH values strength was reduced, and after adjustment to pH 2.0 the chrome leathers had lost nearly 20%, and the vegetable, semichrome, and retan leathers between 30% and 40%, of their strength. Percentage changes in strength of replicates varied by ± 15%.

The shrinkage temperature of the retan and semichrome leathers was little affected by the treatment, but that of the vegetable and chrome leathers was reduced by the two most acid treatments (Table II). The shrinkage temperature of the chrome leather also decreased as the pH of the leather was raised above 5.0 (*see also Bowes and Moss* [8]). There was some indication that the semichrome and retan leathers were similarly affected at the highest pH.

Effect of moist storage.—In spite of the addition of p-nitrophenol to the solutions used in adjusting the pH, varying degrees of mold growth were observed on the leathers after six weeks. In general, this was most prevalent at the intermediate pH values and on the vegetable-tanned leathers. The mold was removed from the leathers, and beakers of toluene were placed in the storage vessels. This checked any further extensive growth of mold.

During storage the pH of the leathers tended to revert toward the original pH of the leather (*see Table I*), presumably because equilibrium had not been reached during the treatments. With the chrome, semichrome, and retan leathers the changes probably also reflect changes in the chrome complex.

Appearance of leathers.—The appearance of the chrome leather was not appreciably affected by the storage, except for a slight enhancement of the green tinge observed after adjustment to the more alkaline pH values. The most acid vegetable and retan leather showed signs of extensive damage and had to be removed after two and six weeks' storage respectively. These samples were darkened in color, hard, and brittle, and the middle layer was dark and glassy in appearance and had lost all fiber structure. In general, the darkening in color and increased stiffness observed after the

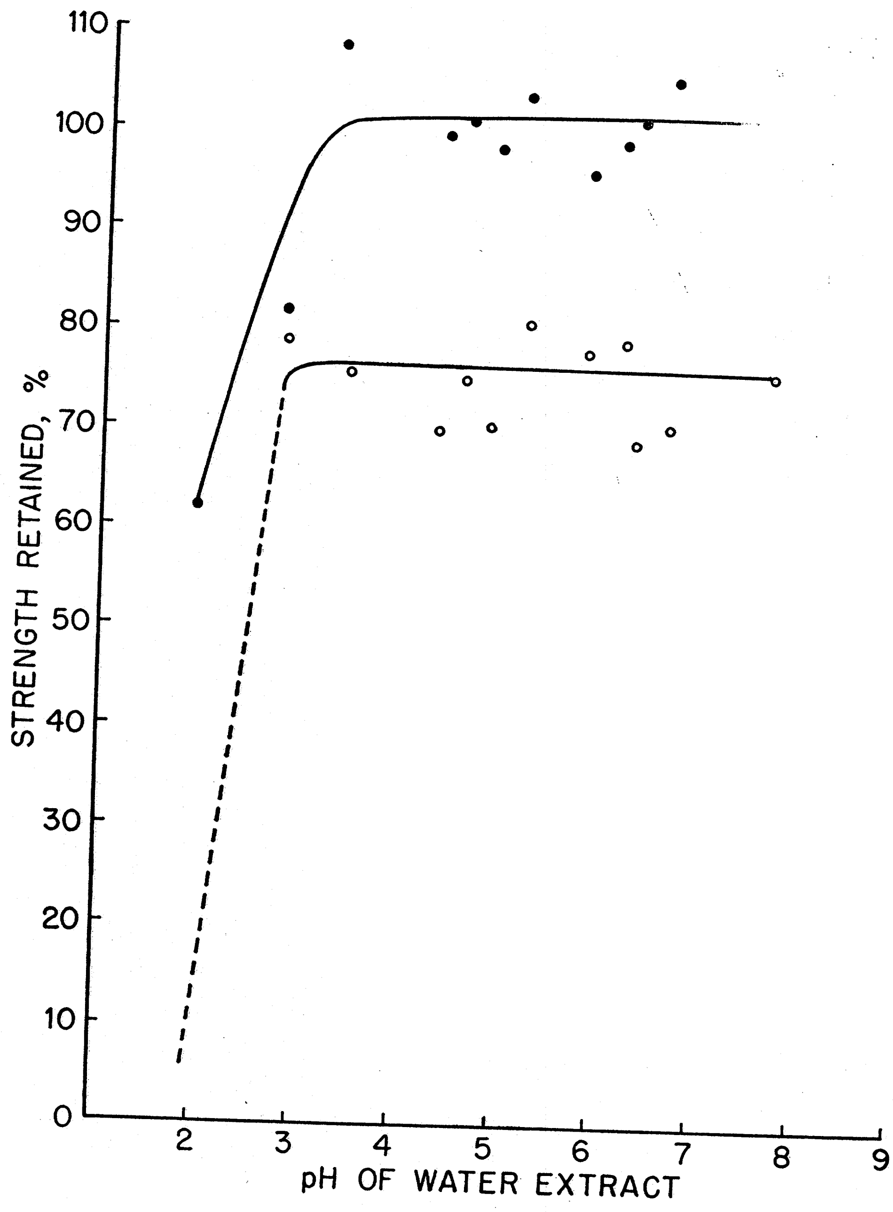

FIGURE 1.—Influence of pH on strength. Vegetable-tanned leather.

●———● Changes in strength on adjustment of pH. Buckle tear load after treatment as a percentage of buckle tear load of original leather.

○———○ Changes in strength on moist storage at 40°C. Buckle tear load after storage as a percentage of buckle tear load before storage.

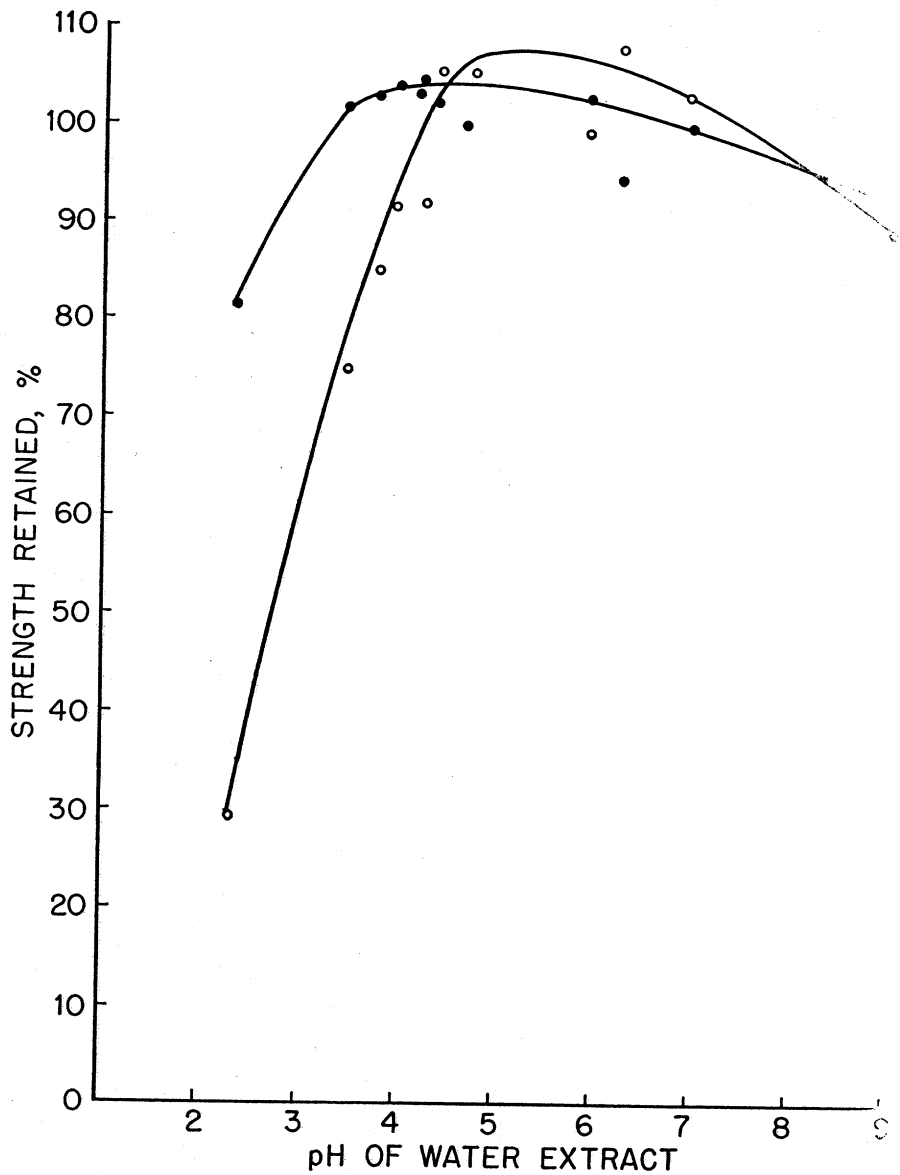

FIGURE 2.—Influence of pH on strength. Chrome-tanned leather.

●———● Changes in strength on adjustment of pH. Buckle tear load after treatment as a percentage of buckle tear load of original leather.

○———○ Changes in strength on moist storage at 40°C. Buckle tear load after storage as a percentage of buckle tear load before storage.

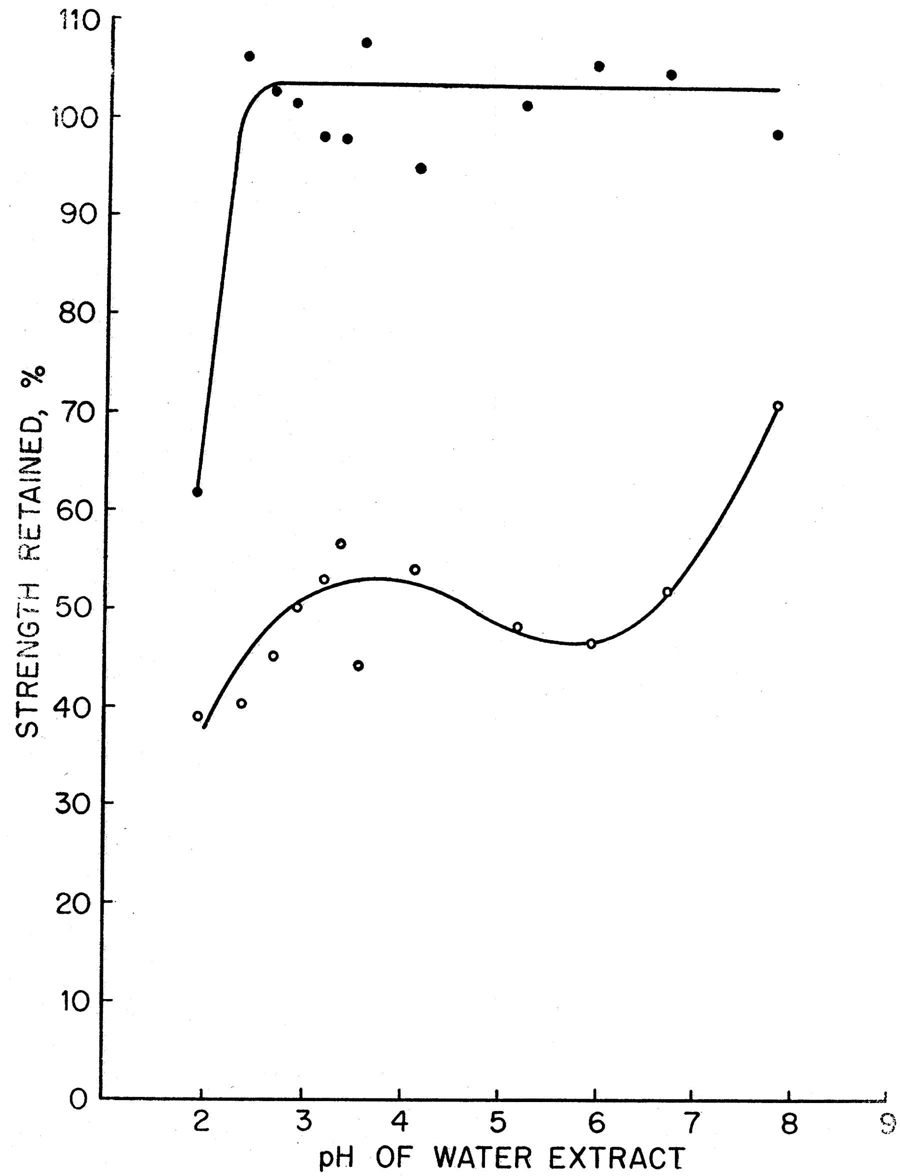

FIGURE 3.—Influence of pH on strength. Semichrome leather.

●——● Changes in strength on adjustment of pH. Buckle tear load after treat ment as a percentage of buckle tear load of original leather.

○——○ Changes in strength on moist storage at 40°C. Buckle tear load after storage as a percentage of buckle tear load before storage.

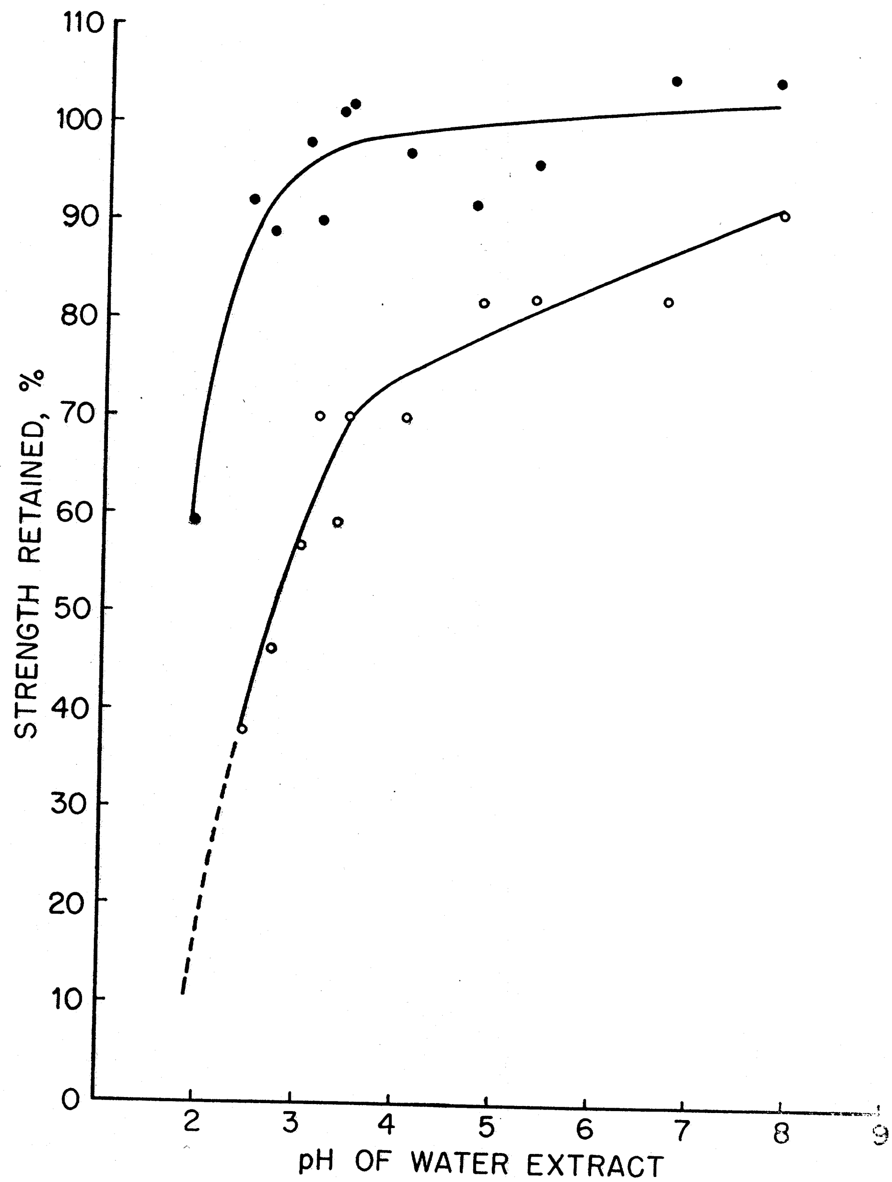

FIGURE 4.—Influence of pH on strength. Chrome retan leather.

●——● Changes in strength on adjustment of pH. Buckle tear load after treatment as a percentage of buckle tear load of original leather.

○——○ Changes in strength on moist storage at 40°C. Buckle tear load after storage as a percentage of buckle tear load before storage.

TABLE II

CRACKINESS AFTER STORAGE

Treatment	Vegetable	Chrome	Semichrome	Retan
1. N HCl	+++++ very damaged	0	++++	+++++ very brittle
2. $0.2N$ HCl	+	0	++	++
3. $0.1N$ HCl	0	0	++	++
4. Water	0	0	+	+
5. $0.05N$ Na_2CO_3	0	0	+	++
6. $0.1N$ "	0	0	+	++
7. $0.15N$ "	0	0	++	++
8. $0.25N$ "	++	0	+++	+
9. $0.4N$ "	+	0	+++	+
10. $0.6N$ "	+	0	++++	++
11. $0.8N$ "	++	0	++++	++
12. $1.5N$ "	++++	+	++++	++

0 = not cracky
+ — ++++++ = "very slightly" increasing to "very cracky"

more alkaline treatments were accentuated by storage, and in many cases the leathers had become cracky (*see Table II*).

The chrome leather showed no tendency to crack except at the highest pH value. The most acid vegetable, semichrome, and retan leathers were all very cracky. The vegetable-tanned leather tended to become cracky at pH values above about 5.0, but only the most alkaline leather was very cracky. All the semichrome and retan leathers developed some degree of crackiness; the semichrome was the most affected, and as the pH rose above 4.0 it became increasingly cracky.

Shrinkage temperature.—As in previous experiments the shrinkage temperature of the vegetable-tanned leather tended to increase slightly during storage (1,2), but there was no evidence that this increase was affected by pH. The changes in shrinkage temperature of the chrome leather were somewhat erratic, but in most cases there was a rise. The shrinkage temperature of both the semichrome and retan leathers fell markedly during storage. The semichrome leathers were the most affected, the fall in shrinkage temperature generally being about 16°, increasing to 23° at the highest pH and to as much as 49° at the lowest pH. With most of the retan leathers falls were between 10° and 16°, increasing to 36° at the lowest pH and becoming negligible above pH 4.5.

Buckle tear load.—The strength retained after storage, expressed as percentage of the strength immediately after adjustment of the pH, is plotted against the pH of the leathers in Figs. 1 to 4. Replicates again varied by ±15%.

TABLE III

CHANGE IN SHRINKAGE TEMPERATURE DURING STORAGE, °C.

Treatment	Before	After	Change	Before	After	Change
		Vegetable			*Chrome*	
1. *N* HCl	60	62	+2	96	97	+1
2. 0.2*N* HCl	69	73	+4	106	108	+2
3. 0.1*N* HCl	77	76	−1	110	110	0
4. Water	77	78	+1	110	107	−3
5. 0.05*N* Na_2CO_3	79	81	+2	112	106	−6
6. 0.1*N* "	77	81	+4	112	108	−4
7. 0.15*N* "	77	82	+5	114	111	−3
8. 0.25*N* "	79	82	+3	108	113	+5
9. 0.4*N* "	78	83	+5	101	111	+10
10. 0.6*N* "	78	81	+3	95	106	+11
11. 0.8*N* "	76	79	+3	88	94	+6
12. 1.5*N* "	77	74	−3	63	70	+7
		Semichrome			*Chrome Retan*	
1. *N* HCl	109	66	−49	98	62	−36
2. 0.2*N* HCl	109	88	−21	97	77	−20
3. 0.1*N* HCl	109	93	−16	96	82	−14
4. Water	108	94	−14	96	86	−10
5. 0.5*N* Na_2CO_3	109	93	−16	96	86	−10
6. 0.1*N* "	109	93	−16	98	86	−12
7. 0.15*N* "	110	94	−16	100	84	−16
8. 0.25*N* "	109	95	−14	100	88	−12
9. 0.4*N* "	110	95	−15	99	91	− 8
10. 0.6*N* "	111	92	−19	96	96	0
11. 0.8*N* "	110	88	−22	94	94	0
12. 1.5*N* "	104	81	−23	93	86	− 8

The strength of the chrome leathers adjusted to pH values between 4.5 and 7.0 was little affected by storage, but losses in strength increased progressively with fall in pH below 4.5 until at pH 2.2 the leather only retained 30% of its strength before storage. There was also some loss in strength at the highest pH value.

Losses in strength of the vegetable-tanned leather were unaffected by variations in the pH in the range 2.5 to 8.0, fluctuating between 20% and 30%. Although adjustment of the pH to 2.8 in itself caused a marked reduction in strength, the further reduction on storage was only of the same order as that at the higher pH values. The deleterious effect of higher acidities was, however, apparent at pH 2.0, the leather being extensively damaged after only two weeks' storage.

The behavior of the semichrome leather was also relatively unaffected by pH, and even at the lowest pH value losses in strength were only slightly greater than at the high values. The smaller loss in strength at the highest pH requires further investigation. With the retan leather losses of strength increased with decrease in pH over the whole range, slowly at first and then more rapidly below pH 4.0. As with the vegetable-tanned leathers the combined effect of adjustment to pH 2.0 and storage led to extensive loss of fiber structure and the collapse of the leather during storage.

Solubility in 5*M* acetic acid.—As in the previous investigation (2) the nitrogen extracted by 5*M* acetic acid was relatively small except with the most damaged leathers. With the vegetable, semichrome, and retan leathers both volatile and nonvolatile nitrogen were greatly increased by

TABLE IV

SOLUBLE NITROGEN

(*Nitrogen extracted by* 5M *acetic acid as percent total nitrogen*)

Treatment	Vegetable		Chrome		Semichrome		Chrome Retan	
	Volatile	Non-Volatile	Volatile	Non-Volatile	Volatile	Non-Volatile	Volatile	Non-Volatile
Original leather before storage	1.11	0.61	0.70	0.14	0.37	0.15	0.58	0.57
1. *N* HCl	3.77	14.49	0.60	0.44	1.08	6.03	2.12	27.39
2. 0.2*N* HCl	0.21	0.76	0.25	0.19	0.64	0.84	0.25	2.48
7. 0.15*N* Na_2CO_3	0.12	0.14	0.11	0.25	0.08	0.21	0.19	0.30
12. 1.5*N* Na_2CO_3	0.09	0.17	0.07	1.18	0.21	0.68	0.05	0.11
Same leather after storage for 12 weeks at 40°C. (no treatment—taken from ref. [2])	0.27	0.48	0.16	0.20	0.51	0.61	0.98	0.46
Same leather after storage for 10 weeks at 60°C. (from ref. [2])	1.40	19.8	1.55	1.50	4.36	11.76	4.25	24.4

storage at the lowest pH value (*ca.*2.0) but only slightly increased at the next lowest pH (*ca* 2.5–2.7). Of these the retan leather was the most affected, and the semichrome the least. The amounts extracted from the leather of pH 2.0 were of the same order as those extracted from the original leathers when stored for a similar period at 60°C. (2). The solubility of the chrome leather was not greatly affected by the pH of the leather during storage except for a slight increase with the leathers of lowest and highest pH.

DISCUSSION

The adjustment of the pH had some effect on the properties of the leather, increase in pH causing darkening and stiffening of the leathers containing vegetable tans and decrease in pH causing some loss in strength. Except with the most acid leather, however, these changes were small compared with those occurring during storage.

The pH of the leathers had less effect on the changes taking place during storage than was expected. Only with the retan leathers did losses in strength decrease consistently with increase in pH over the whole range covered. With the chrome leathers the effect of pH was only obvious below pH 4.0; with the vegetable-tanned leather, only at the lowest pH; and with the semichrome leathers, it had only a slight effect even at pH 2.0.

Although increase in pH above 4.0 had little effect on the strength of vegetable and semichrome leathers, it had an adverse effect on their color and increased their tendency to develop crackiness, especially the semichrome leathers. The retan leather also darkened with rise of pH, but there was little variation in crackiness.

The effect of pH on the fall in shrinkage temperature of the semichrome and retan leathers is of interest. With leathers of low pH the falls are very great, resulting in final values approaching the danger level. The shrinkage temperature of the semichrome leathers also fell by about 20° at the two highest pH values, but in contrast that of the retan leathers of pH 4.5 and above fell little, if at all.

The increased solubility of the leathers in acetic acid solutions suggest that hydrolytic breakdown has been increased by lowering the pH, though with the chrome leathers this increase is relatively small.

How far these results are applicable to other vegetable, chrome, semichrome, and chrome retan leathers is not certain, but they give some indication of the pH range likely to give optimum resistance to moist heat. These vary slightly with the leather. With chrome leather it would seem that it is desirable to have a pH of water extract in the range 4.5 to 6.0. With the leathers containing vegetable tan, the upper pH is limited by the tendency to crackiness, particularly with the semichrome leathers. With vegetable-tanned leathers and semichrome leathers the pH should not fall below 3.0, and with retan leathers it should be as high as is consistent with a good color. The pH, however, is likely to change in wear; exposure to moist heat generally causes the pH to fall (1, 2), especially with semichrome and retan leathers, while absorption of perspiration may cause the pH to rise. The pH at which to aim will, therefore, be to some extent dependent on the purpose for which the leather is required.

As in previous investigations (1) chrome leather appears to be the most resistant to moist heat, changes but slightly in appearance, has little tendency to become cracky, and provided the pH is above 4.5, has small losses in strength. Chrome leather is, however, more susceptible to the detanning action of perspiration, and in some circumstances where perspiration is likely to be an important factor semichrome or retan leathers may be preferable.

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